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Optical properties of semiconductor (InP)–dielectric quantum wires

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The absorption and luminescence spectra of InP embedded in chrysotile asbestos nanotubes have been explained in terms of exciton transitions in semiconductor – dielectric quantum wires (S–D QWRs). The features of the time-resolved luminescence of porous InP have been explained by numerous physical processes in S–D QWRs or quantum dots (QDs): slowing down of intraband relaxation in one-dimensional energy band of QWRs or excess energy of holes in QDs, collective exciton–exciton (electron) interaction in nanostructures, Auger recombination etc.

In quantum wires, consisting of semiconductor and dielectric components, Coulomb attraction between electron and hole inside semiconductor filaments may be considerably enhanced. Qualitatively it can be explained resorting to the electric lines of forces that connect electron-hole pair. They propagate partially outside the semiconductor filament in dielectric with $\varepsilon_d \ll \varepsilon_s$ ($\varepsilon_{d,s}$ — dielectric constants of dielectric and semiconductor). Thus it is possible to change the binding energy and the oscillator strength of QWRs constituting semiconductor filaments and dielectric matrix with different dielectric constants — realizing Coulomb interaction engineering [1].

Chrysotile asbestos is a natural material that consists of the bundles of closely packed parallel transparent dielectric up to a few μm long nanotubes. The internal and external diameters of nanotubes of the samples, measured using the electron microscope, were 4–5 nm and 30 nm². The standard atmospheric pressure MOCVD reactor [2] has been used to grow crystalline InP inside nanotubes³.

The absorption spectrum (Fig. 1) of the InP crystallized in chrysotile asbestos has a well pronounced band with maximum at 1.9 eV that we attribute to the absorption of nanostructures. This spectrum has been obtained using optical microscope to choose the 2 μm diameter area of the sample. We account the monotonous increase of absorption at higher energies (the background) to the absorption of the bulk InP that may be crystallized at the surface of the bunches of nanotubes and to the absorption of chrysotile asbestos matrix.

The luminescence of InP embedded in chrysotile asbestos excited by 14 ns polarized pulses of the second harmonic ($\hbar\omega = 2.39 \text{ eV}$) of Al-Y laser has been investigated using polychromator with 0.01 eV spectral resolution. The maximum intensity of excitation was 4 MW/cm². The spectra have two wide bands. We attribute the band with maximum at about 1.9 eV to the luminescence of nanostructures and the broad band (with much weaker intensity) at higher energies to the luminescence of the matrix. The latter is confirmed by the measurement of pure chrysotile asbestos matrix luminescence. The luminescence

²Measurements were done by N. A. Kiselyov and D. N. Zakharov at Institute of Crystallography.

³We are much indebted to M. Pemble and H. M. Yates for supplying the samples for our experiments

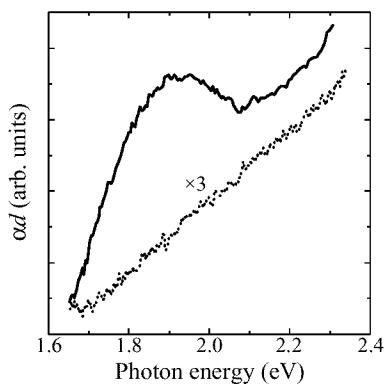


Fig. 1. The absorption spectra of InP QWRs crystallised in chrysotile asbestos nanotubes (solid line) and chrysotile asbestos matrix (dashed line).

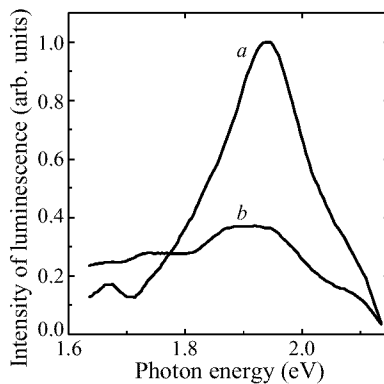


Fig. 2. The PL spectra of InP QWRs crystallised in chrysotile asbestos nanotubes at different polarization of exiting light parallel (a) and perpendicular (b) to the axis of nanotubes.

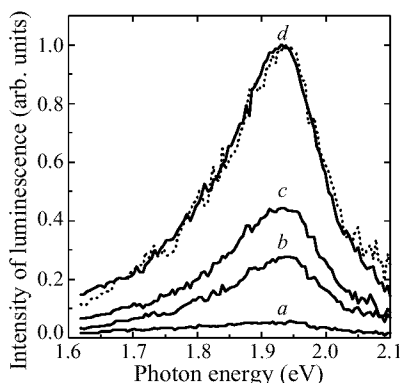


Fig. 3. The PL spectra of InP QWRs crystallised in chrysotile asbestos nanotubes at different intensities of excitation: (a) $I = 0.13 \text{ MW/cm}^2$; (b) $I = 0.95 \text{ MW/cm}^2$; (c) $I = 1.64 \text{ MW/cm}^2$; (d) $I = 4.73 \text{ MW/cm}^2$ and dashed line — spectrum (a) $\times 17$.

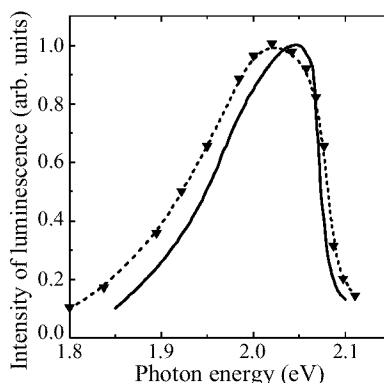


Fig. 4. The normalised PL spectra of porous InP at two intensities of excitation: $I = 150 \text{ MW/cm}^2$ (dashed line); $I = 400 \text{ MW/cm}^2$ (solid line).

spectra presented in this paper were obtained by subtracting the luminescence spectra of the pure chrysotile asbestos from the luminescence spectra of InP embedded in chrysotile asbestos. The independence of the halfwidth of the luminescence spectra ($\approx 0.18 \text{ eV}$) upon the intensity of the exciting laser beam allows us to suppose that InP has been crystallized in the form of nanostructures inside the chrysotile asbestos nanotubes because the density of QDs and QWRs states differs from that of the bulk semiconductor. The essential difference of the luminescence intensity for parallel and perpendicular polarization of the exciting laser beam (Fig. 2) enables us to suppose that the luminescence of InP S-D QWRs dominates for our samples. This difference in the luminescence intensity may be explained by the anisotropy of absorption - by the modification of the electromagnetic field eigenmode in the vicinity of QWRs [3] In QWRs the exciton transitions play the dominant role [4]

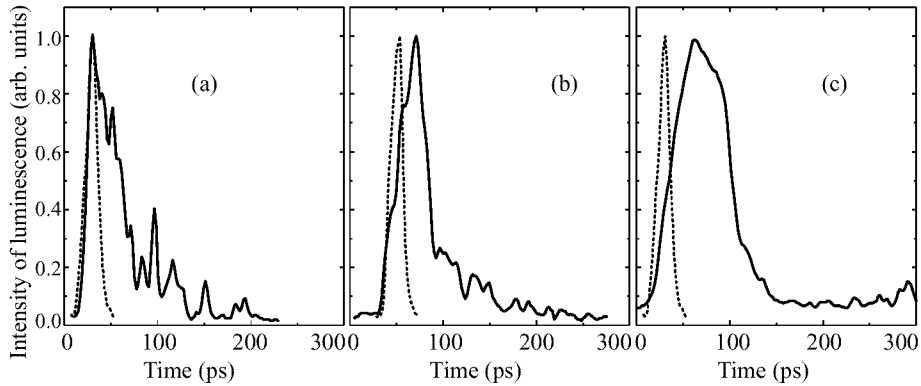


Fig. 5. The resolved intensity of porous InP at three levels of excitation by picosecond laser pulses: (a) low ($I = 80 \text{ MW/cm}^2$); (b) medium ($I = 270 \text{ MW/cm}^2$); (c) high ($I = 400 \text{ MW/cm}^2$). The laser pulse is shown by dashed lines.

so we attribute the 1.9 eV luminescence and absorption bands to the exciton transitions in InP (semiconductor) – chrysotile asbestos (dielectric) quantum wires. The measured energy of exciton transitions ($\sim 1.9 \text{ eV}$) in 4–5 nm InP S–D QWRs corresponds to that calculated using a variation technique accounting for the effect of dielectric enhancement in the cylindrical QWRs [5].

The samples of porous InP have been obtained by electrochemical etching of n-InP(100) substrate. The time resolved luminescence of porous n-InP excited by picosecond pulses of the second harmonic ($\hbar\omega = 2.34 \text{ eV}$) of Nd-glass laser (pulse duration about 10–14 ps) has been investigated using streak camera with 5–10 ps resolution. The luminescence spectra of porous InP (broad band $2.07 \pm 0.04 \text{ eV}$, Fig. 4) excited by powerful picosecond pulses are shifted to the blue spectral region compared with that of the bulk. This shift allows us to estimate the average size of nanostructures: the diameter is about 5 nm (3.4 nm) if the luminescence of QDs (QWRs) is assumed. In the latter case the dielectric enhancement of excitons in S–D QWRs has been taken into account.

The kinetic properties of the intensity of luminescence differ for low and high levels of laser excitation (Fig. 5). For low intensities of excitation ($I < 250 \text{ MW/cm}^2$, Fig. 5(a)) the luminescence is characterized by exponential decay and very short rise time. With increasing of excitation the rise time of luminescence grows up (Fig. 6). When the intensity of excitation exceeds 250 MW/cm^2 the additional fast decay arises (Fig. 5(b)). For the highest excitation level the decay of luminescence has three typical parts: the relatively slow relaxation is followed by fast fall and then by slow relaxation (Fig. 5(c)). The slow decay of luminescence at low intensities of excitation (Fig. 5(a)) and the final slow part at high intensities (Fig. 5(c)) might be attributed to the linear recombination of excitons. The insignificant narrowing of the luminescence spectrum at high excitation allows us to exclude the contribution of the stimulated emission and explain the fast part of the decay (Fig. 5(b, c)) by exciton–exciton (electron) interaction and Auger nonradiative recombination.

The appearance of the initial relatively slow part of the decay at high excitation (Fig. 5(c)) and the increasing of the luminescence rise time with the increasing of the excitation level may be explained by the slowing down of intraband relaxation in semiconductor QWRs (hole excess energy relaxation in semiconductor QDs) at high density of the excited carriers because of the screening of electron–phonon interactions and the saturation of phonon

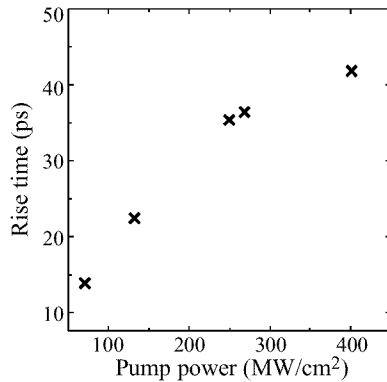


Fig. 6. The dependence of the porous InP rise time upon the pumping intensity.

modes [6]. Thus the intraband relaxation time becomes comparable with the recombination time, and the relatively slow recombination of excitons may be followed by fast decay due to the exciton–exciton, exciton–electron interaction or Auger nonradiative recombination when considerable quantity of quasiparticles is accumulated.

Acknowledgments

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